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## Interfacial thermal conductance between monolayer WSe<sub>2</sub> and SiO<sub>2</sub> with consideration of radiative electron-hole recombination

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**Interfacial thermal conductance between monolayer WSe<sub>2</sub> and SiO<sub>2</sub> with consideration of  
radiative electron-hole recombination**

by

**Nicholas Hunter**

A thesis submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee:  
Xinwei Wang, Major Professor  
Jonathan Claussen  
Yue Wu

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2020

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**NOMENCLATURE**

$\beta$	radiative recombination efficiency
CW	continuous wave
$G$	interfacial thermal conductance
ns	nanosecond
PL QY	photoluminescence quantum yield
ps	picosecond
RSC	Raman shift coefficient
TMD	transition metal dichalcogenide

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## ABSTRACT

This work reports the interfacial thermal conductance ( $G$ ) and radiative recombination efficiency ( $\beta$ ) – also known as photoluminescence quantum yield (PL QY) – of monolayer WSe<sub>2</sub> flakes supported by fused silica substrate via state-resolved energy transport Raman (ET-Raman). This is the first known work to consider the effect of radiative electron-hole recombination on the thermal transport characteristics of single layer transition metal dichalcogenides (TMDs). ET-Raman uses a continuous wave laser for steady state heating as well as nanosecond and picosecond lasers for transient energy transport to simultaneously heat the monolayer flakes and extract the Raman signal. The three lasers induce distinct heating phenomena that distinguish the interfacial thermal conductance and radiative recombination efficiency which can then be determined in tandem with 3D numerical modeling of the temperature rise from respective laser irradiation. For the five samples measured,  $G$  is found to range from  $2.10 \pm 0.14$  to  $15.9 \pm 5.0$  MW m<sup>-2</sup> K<sup>-1</sup> and  $\beta$  ranges from  $36 \pm 6$  to  $65 \pm 7$  %. These values support the claim that interfacial phenomena such as surface roughness and 2D material-substrate bonding strength play critical roles in interfacial thermal transport and electron-hole recombination mechanisms in TMD monolayers. It is also determined that low-level defect density enhances the radiative recombination efficiency of single layer WSe<sub>2</sub>.

## CHAPTER 1. INTRODUCTION

Transition metal dichalcogenides (TMDs) 2D materials are attracting significant research attention for their unique electrical and optical properties. Some of these remarkable properties include tunable bandgaps, large exciton binding energy, and strong photoluminescence as monolayers due to their indirect to direct bandgap transition as the 2D material thickness decreases to single layer <sup>1-3</sup>. A wide range of potential applications exist for these novel 2D materials including integrated circuitry, optoelectronics, spintronics, and field effect transistors <sup>4-7</sup>. The increased photoluminescence as monolayers make TMDs particularly suitable for atomic scale light emission devices <sup>8</sup>.

Before 2D TMDs can be incorporated as reliable materials for modern technology needs and green energy solutions a proper understanding of heat dissipation at the nanoscale is critical. The thermal resistance in nanoscale devices dictates overall performance and can severely limit the operation of electronic systems. In particular, the interfacial thermal conductance ( $G$ ) between a 2D material and its substrate is subject to numerous factors such as surface roughness, compositional disorder, atomistic dislocations, and interfacial bonding <sup>9</sup>. The variability of interface phenomena and the atomic-level thickness of 2D TMDs make precise characterization of interfacial thermal transport challenging.

Researchers have employed optical, electrical, and computational techniques to study the interfacial thermal conductance between thin film TMDs and substrates. Comparison of recent works reveals moderate to substantial discrepancies between reported results. Yasei et al.<sup>10</sup> used electrical thermometry and subsequent 3D finite element analysis to characterize thermal transport across monolayer MoS<sub>2</sub> and SiO<sub>2</sub>/Si substrate to conclude a thermal boundary conductance of 20.3–33.5 MW m<sup>-2</sup> K<sup>-1</sup>. For comparison, Zhang et al.<sup>11</sup> measured a thermal

conductance to be of the order  $0.1 - 1 \text{ MW m}^{-2} \text{ K}^{-1}$  using a refined optothermal Raman technique on single and bilayer  $\text{MoS}_2$  and  $\text{MoSe}_2$ . On the computational and theoretical side, the acoustic mismatch model (AMM)<sup>12</sup>, diffuse mismatch model (DMM)<sup>13</sup>, and molecular dynamics simulations<sup>14</sup> are commonly used to predict  $G$ . Correa et al.<sup>15</sup> developed a first principles model for interfacial phonon transport to predict a larger  $G$  of  $\sim 10^8 \text{ W m}^{-2} \text{ K}^{-1}$  between monolayer  $\text{MoS}_2$  and amorphous  $\text{SiO}_2$  and proposed that large surface variation or sharp atomic-scale features between sample and substrate decrease overall conductance across an interface. The 1~2 orders of magnitude difference for reported  $G$  values of  $\text{MoS}_2$  monolayers suggest a need for more refined interfacial thermal conductance measurement techniques.

Raman-based thermal probing techniques using steady state lasers are employed frequently to study thermal properties of 2D materials<sup>16-19</sup>. However, the optothermal Raman technique requires calibration of a Raman temperature coefficient and precise determination of laser absorption – both of which are subject to non-negligible error that could impact final experimental results. As thoroughly detailed by Xu et al.<sup>20</sup>, thermal expansion mismatch between sample and substrate during calibration introduces stress distinct from the stress involved from laser heating during Raman probing. Therefore, relying on temperature coefficients determined during calibration may introduce unknown error when using Raman spectroscopy to measure sample temperature change. Additionally, laser absorption measurements can be affected by interfacial spacing which causes Raman intensity enhancement due to multiple reflections at the interface gap<sup>21</sup>. Optical absorption measurements then become sample specific since interface spacing between 2D material and substrate can vary depending on thickness of the sample and



preparation method<sup>22</sup>. Laser absorption coefficients are often estimated from models or borrowed from others' work introducing further uncertainty to Raman-based temperature measurements<sup>17,18</sup>.

The radiative recombination of electron-hole pairs further complicates experimental measurements of interfacial thermal conductance. Because monolayer TMDs have a direct band gap, laser excited electrons in the conduction band have a probability of recombining radiatively with holes in the valence band (i.e. photon emission). This means that not all the laser energy absorbed in the sample converts to thermal energy in the form of phonons or hot electrons<sup>23</sup>. This critical feature of monolayer TMDs has never been considered while studying interfacial conductance via Raman based thermal probing with laser heating. A full physics understanding of local interface energy coupling requires consideration of the radiative recombination effect in single layer TMD materials.

In this work we report the interfacial thermal conductance of monolayer tungsten diselenide (WSe<sub>2</sub>) on fused silica (SiO<sub>2</sub>) substrate with consideration of radiative recombination physics. In recently published work, we have extensively detailed a novel technique – energy transport state-resolved Raman (ET-Raman) – that eliminates uncertainty introduced by laser absorption measurements and Raman temperature calibration required in most Raman-based thermal measurements. ET-Raman involves differentiating the thermal energy transport mechanism for a sample under laser heating by changing laser sources from continuous wave (steady state) to pulsed laser (transient heat conduction). In this work we use continuous wave (CW) and nanosecond (ns) lasers in conjunction with 3D numerical modeling to simulate temperature rises of the laser heated sample area and determine the interfacial thermal conductance  $G$ . Once  $G$  is determined, we introduce a picosecond (ps) pulsed laser to determine

the radiative recombination coefficient ( $\beta$ ). Because the average excited carrier lifetime of monolayer WSe<sub>2</sub> is much longer than the picosecond pulse width (13 ps), no electron-hole pairs have time to recombine during pulse heating. Thus, heating of the sample during the picosecond pulse only consists of thermal energy in the form of phonons during the fast thermalization process. By distinguishing multiple energy transport states – two where radiative recombination occurs (CW and ns) and one where it does not (ps) – the proportion of electron-hole pairs that recombine radiatively can be determined.

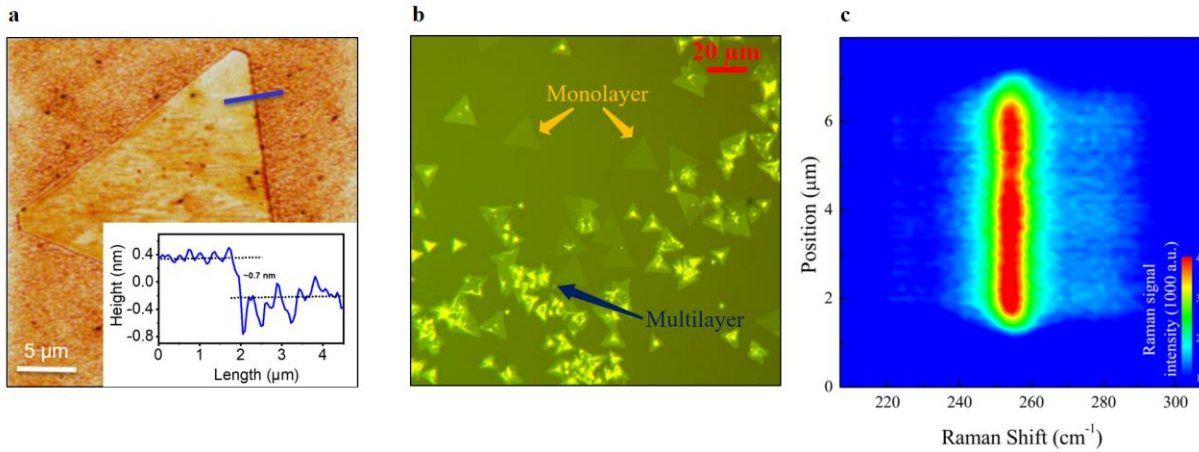
## CHAPTER 2. EXPERIMENTAL DETAILS

### 2.1 Sample Preparation and Characterization

The 2D crystals were prepared by the laser-assisted synthesis technique (LAST)<sup>24</sup>, where the high-quality monolayer WSe<sub>2</sub> crystals were directly synthesized from the stoichiometric powder. Stoichiometric WSe<sub>2</sub> powder was placed inside a custom-made graphite crucible (1.2×0.7×0.7 cm<sup>3</sup>), and subsequently, a CW CO<sub>2</sub> laser with 10.6 μm wavelength was used to heat the graphite crucible to evaporate the WSe<sub>2</sub> powder. Transparent fused silica was used as the growth substrate. The substrate was placed face down on top of the graphite crucible at a 6 mm distance inside a 1-inch furnace tube. Due to chemically inert and low heat conductivity attributes, Argon gas was used as the background gas to adjust the growth pressure to 150 torr. Before starting the growth process, the furnace tube was vacuumed, followed by an argon flow to flush the residual remains of air molecules. After adjusting the furnace temperature to 800°C, the growth process was initiated by irradiating the graphite crucible at 35 W laser power for 50 seconds. Right after finishing the irradiation process, the vacuum environment was kept active until the furnace was naturally cooled down to room temperature.

The LAST method produces high quality WSe<sub>2</sub> monolayer flakes well-suited for optothermal Raman measurements. Atomic force microscopy (AFM) imaging measured the thickness of the monolayers to be approximately 0.7 nm (**Figure 1a**). The line profile in the AFM image shows a smooth surface on the WSe<sub>2</sub> monolayer relative to the fused silica substrate. Because the LAST method produces an abundance of monolayer as well as few-layered samples, the distinction between them is shown in **Figure 1b**. Monolayers exhibit a uniform surface and appear only slightly distinguished from the underlying substrate. The few-layered samples appear brighter and display more variation on their surfaces. Measured from the vertex to the

opposite base of a triangular flake, monolayer samples measure  $\sim 13 \mu\text{m}$  across. In order to study the structural uniformity of the monolayers, Raman measurements were collected in a 1D line scan across the surface of a sample. As can be seen in **Figure 1c**, the Raman signal strength remains constant over the entire length of the sample suggesting a high degree of structural uniformity.



**Figure 1.** Images detailing the structural characterization of the  $\text{WSe}_2$  monolayer samples. (a) The AFM image of a single monolayer flake with the accompanying line profile shows a sample height of  $\sim 0.7 \text{ nm}$ . Note the surface roughness transition from the  $\text{WSe}_2$  area to the fused silica substrate; the fused silica demonstrates noticeably higher levels of surface roughness. (b) The optical image shows representative monolayer samples, slightly pronounced from the underlying substrate. From the base of the triangular flake to the opposite vertex the monolayers measure approximately  $13 \mu\text{m}$ . Multilayer samples show more variation at the surface and appear brighter. (c) Raman measurements collected as a 1D line scan across the surface of a monolayer sample demonstrate the structural uniformity of  $\text{WSe}_2$ . The line scan was measured along an  $8 \mu\text{m}$  distance with Raman measurements taken at  $0.1 \mu\text{m}$  intervals. The constant Raman signal intensity during the line scan suggests uniform structural characteristics.

## 2.2 Interfacial Thermal Characterization: Physics

In the ET-Raman technique, different energy transport states (in spatial and time domains) are constructed. This is intended to distinguish different physical transport processes in the material. In the past, we have used this technique to distinguish the in-plane heat conduction, interface thermal conduction, and in-plane hot carrier diffusion of supported and suspended 2D materials including  $\text{MoS}_2$ ,  $\text{MoSe}_2$ , and  $\text{WS}_2$ <sup>25–29</sup>.

In this work, we construct three different energy transport states in the time domain (steady, nanosecond, and picosecond) to explore the interface energy transport and electron-hole recombination process. The first step in the ET-Raman process involves laser heating and Raman probing of the WSe<sub>2</sub> monolayers with a CW and ns laser – both with 532 nm wavelength (photon energy of  $E = 2.33$  eV). A 20× objective lens focuses the laser beam on the sample. At this objective, the laser spot size covers most of the triangular crystal of monolayer WSe<sub>2</sub>. Therefore, the in-plane thermal diffusion outside of the laser heating area becomes negligible. The large laser spot size ( $r_o \sim 1.9$  μm) relative to the atomically thin WSe<sub>2</sub> layer ( $\sim 1$  nm) also means the cross-plane phonon transport at the interface dominates over the negligible in-plane heat conduction and hot carrier diffusion <sup>25</sup>.

The hot carrier diffusion length remains the same for all three laser heating scenarios and is evaluated using the formula  $L = \sqrt{D\tau}$  where  $D = 2.2$  cm<sup>2</sup> s<sup>-1</sup> for hot carrier diffusivity and  $\tau = 4$  ns for hot carrier lifetime <sup>30</sup>. This estimate puts the hot carrier diffusion length in the order of 1 μm. Considering the recombination process during diffusion and the relatively large laser spot size, this hot carrier diffusion will have negligible effect on the heat spreading in the in-plane direction <sup>29</sup>. The thermal diffusion length ( $L_T$ ) for CW steady state heating is essentially infinite but can be approximated in this case as 10× the laser spot diameter. In either case, this length is much larger than the atomically thin WSe<sub>2</sub> layer and allows us to assume uniform temperature distribution in the thickness direction ( $z$ -direction).

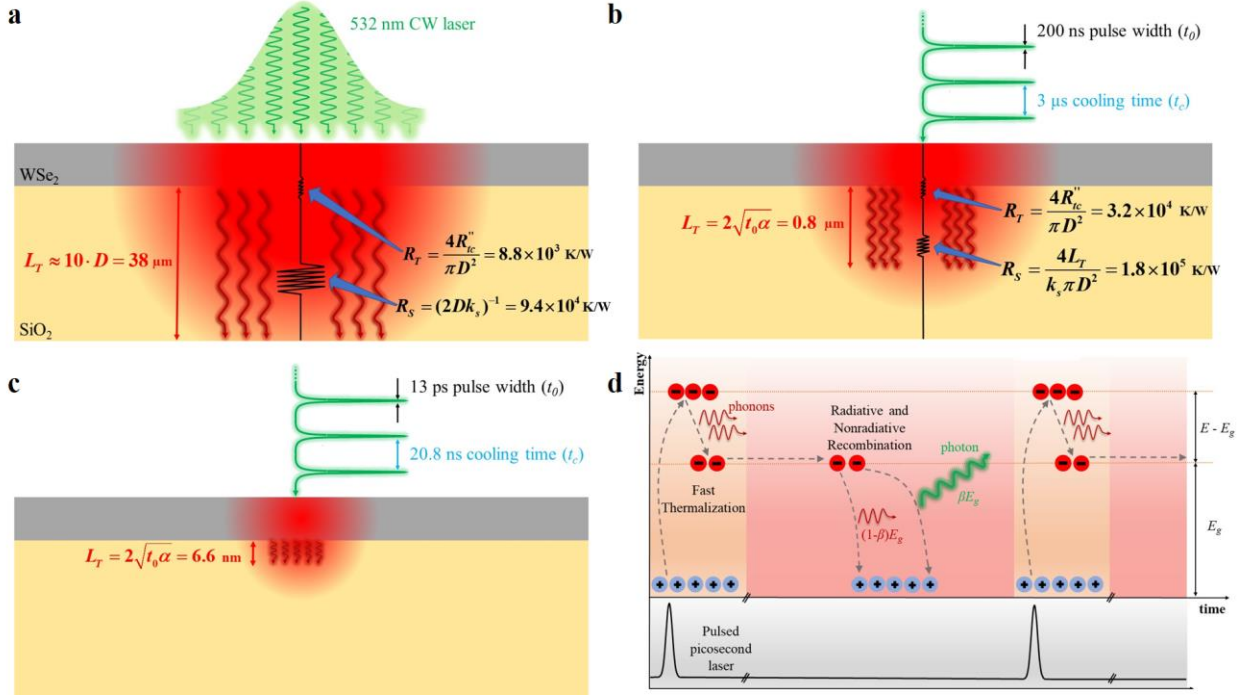
In the CW case, the laser irradiates a WSe<sub>2</sub> monolayer and causes steady state heating. The laser power ( $P$ ) gradually increases while the Raman signal is collected to study the temperature profile. Since the Raman shift location ( $\omega$ ) is redshifted with increasing laser power, we obtain a laser power differential we have called the Raman shift power coefficient (RSC):

$\psi_{CW} = \partial\omega / \partial P$ . The RSC is applied to the degenerate  $A_{1g}$  and  $E_{2g}^1$  first order Raman active modes of monolayer  $WSe_2$  that appear as a single prominent peak around  $250\text{ cm}^{-1}$  in the Raman spectrum<sup>31</sup>. It is important to note that this laser power differential is proportional to laser absorption coefficient ( $\alpha$ ) and Raman temperature coefficient ( $\partial\omega / \partial T$ ), and is also a function of substrate thermal resistance ( $R_s$ ), and interfacial thermal resistance ( $R_{ic}''$ ) – or equivalently  $G^{-1}$ . However, as stated previously, the ET-Raman technique eliminates the effects of laser absorption and Raman temperature coefficient as will be explained in the upcoming section. Therefore, the remaining variables of interest become the already known substrate thermal resistance and the interfacial thermal resistance.

Under CW steady state heating, because of the low thermal conductivity of fused silica the accumulated heating of the substrate disproportionately impacts the overall thermal transport of the system. In other words, the substrate thermal resistance contributes to the measured temperature rise much more than the total interface resistance. Here the substrate resistance is evaluated using the appropriate shape factor for conduction heat transfer through a disk with diameter  $D$  on a semi-infinite medium:  $R_s = 1 / (2Dk_s)$  where  $D$  is the laser spot diameter and  $k_s$  is the substrate thermal conductivity<sup>32</sup>. The total interface resistance is evaluated using  $R_T = 4R_{ic}'' / \pi D^2$  where  $R_{ic}''$  is the interfacial thermal resistance. As shown in this paper, the interfacial resistance is in the order of  $10^{-7}\text{ K m}^2\text{ W}^{-1}$ . Thus, the substrate resistance is significantly larger than the total interface resistance by an order of magnitude:  $9.4 \times 10^4\text{ K W}^{-1}$  and  $8.8 \times 10^3\text{ K W}^{-1}$  respectively (see **Figure 2a**). This means the interface resistance is only 9% of the total substrate resistance. Therefore, the interfacial conductance  $G$  contributes far less to the measured temperature change and has low sensitivity to meaningful measurement. The CW

state serves as a reference state and will be used later in data processing to nullify the effects of laser absorption and Raman temperature coefficient.

In contrast to the CW steady state laser heating, during ns laser heating, the substrate thermal resistance does not dominate the overall thermal transport of the system due to the smaller heat diffusion into the substrate during the pulse heating – as shown in **Figure 2b**. A nanosecond pulsed laser with a 300 kHz frequency repetition rate irradiates the sample. For a pulsed laser the heat diffusion length into the substrate is estimated as  $L_T = 2\sqrt{t_0\alpha}$  where  $t_0 = 200$  ns is the laser pulse width and  $\alpha$  is the thermal diffusivity of the substrate. The diffusion length value for fused silica under nanosecond pulsed laser heating is 0.8  $\mu\text{m}$ . Under these conditions, the substrate thermal resistance is estimated as  $R_S = 4L_T / k_s\pi D^2$  where  $D$  is the ns laser spot diameter (2  $\mu\text{m}$ ). Thus, the substrate resistance value is  $1.8 \times 10^5 \text{ K W}^{-1}$  which is more comparable to the total interface resistance value evaluated as  $3.2 \times 10^4 \text{ K W}^{-1}$  (using the same equation for total resistance as the CW case). The interface resistance now becomes 18% of the total substrate resistance. In the CW case, the substrate resistance effect is more pronounced and masks the presence of the total interface resistance. In the ns case, the total interface resistance influences the thermal transport of the system more prominently.



**Figure 2.** Steady state and zero transport heat conduction in WSe<sub>2</sub> 2D monolayers using continuous-wave, nanosecond, and picosecond lasers. (a) In CW steady state heating, substrate thermal resistance has a larger effect than total interface resistance. Using the appropriate shape factor for conduction heat transfer through a disk with diameter  $D$  on a semi-infinite medium, substrate resistance is calculated as  $R_s = 1/(2Dk_s)$  where  $D = 3.8 \mu\text{m}$  is the diameter of the CW laser spot and  $k_s = 1.4 \text{ W m}^{-2} \text{ K}^{-1}$  is the substrate conductivity. Total interface resistance is calculated as  $R_T = 4R_{ic}''/\pi D^2$ . The thermal diffusion length  $L_T$  is estimated as  $10\times$  the laser spot diameter. (b) During nanosecond pulsed heating, the substrate resistance becomes more comparable to the interface resistance and is more sensitive to measurement. The substrate resistance is evaluated using  $R_s = 4L_T/k_s\pi D^2$  where  $D = 2 \mu\text{m}$  for the nanosecond laser spot size. The total interface resistance is evaluated using  $R_T = 4R_{ic}''/\pi D^2$  where  $L_T$  is the ns heat diffusion length. The heat diffusion length into the substrate is approximately 800 nm – much larger than the sample thickness but smaller than the CW heat diffusion length. (c) For picosecond pulsed heating, the heat diffusion length is only  $\sim 7$  nm. (d) Recombination physics in WSe<sub>2</sub> during pulsed picosecond laser heating. The short laser pulse does not involve e-h recombination. Direct phonon emission is the only source of thermal energy during this time. After the pulse, both nonradiative and radiative recombination occur with respective efficiencies of  $(1-\beta)$  and  $\beta$ .

Like the CW case, laser power increases while Raman signal is collected to obtain the nanosecond Raman shift coefficient ( $\psi_{ns}$ ). At this point, we have two RSC's ( $\psi_{CW}$  and  $\psi_{ns}$ ) representing the laser power differentials applied to Raman shift for two different heating



mechanisms in the sample-substrate system. By taking their ratio, a new parameter is defined called the normalized Raman shift coefficient:  $\Theta_1 = \psi_{ns} / \psi_{CW}$ . This normalized parameter becomes a function of interfacial thermal resistance (i.e. conductance) alone since the Raman temperature coefficient and laser absorption are cancelled out. A finite volume numerical simulation of the heat transfer in both CW and nanosecond cases computes theoretical temperature rises  $\Delta T_{CW}$  and  $\Delta T_{ns}$ . Equating the ratio of the temperature rises to the normalized RSC  $\Theta_1$  allows for precise determination of the interfacial thermal conductance.

Note that both temperatures rises are Raman intensity weighted averages – evaluated over the spatial domain for CW and the spatial-temporal domain for ns. Details of this discussion have been given in our past work <sup>25</sup>. **Figure 3** illustrates the spatial and temporal components involved in the Raman weighted averages for both CW and ns cases. A single ns laser pulse exhibits a Gaussian intensity distribution which must be integrated over space and time (denoted in **Figure**

**3a** as  $\xi_1 = \int_0^t \int_0^V I dv dt$ ). The sample surface temperature multiplied by the weighted intensity values

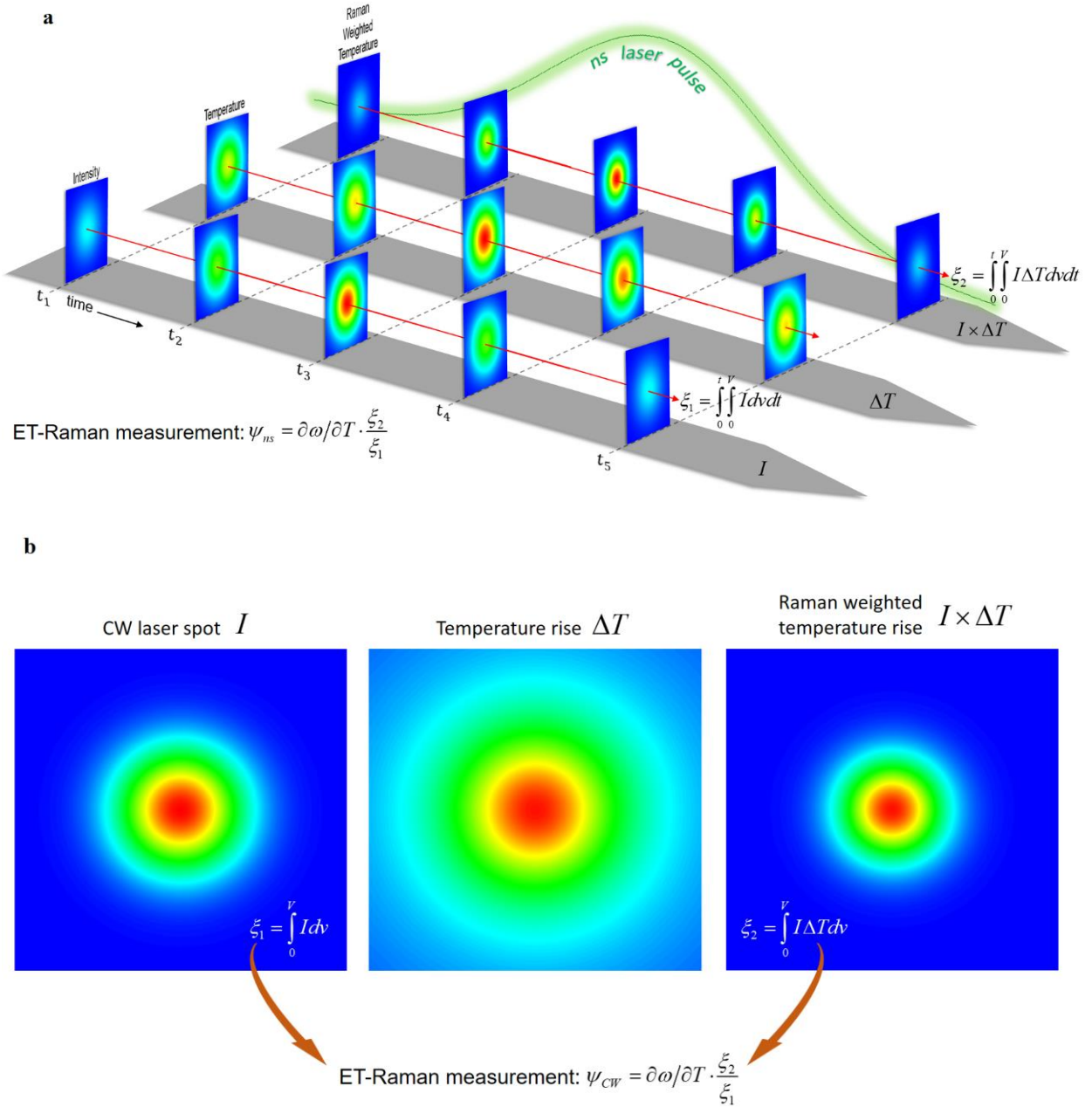
and then integrated over the time and space domain yields the Raman weighted temperature

(denoted in the figure as  $\xi_2 = \int_0^t \int_0^V I \Delta T dv dt$ ). The subsequent Raman weighted average value

representing the experimental temperature rise during ns heating is related to the Raman shift power coefficient  $\psi_{ns} = \partial \omega / \partial T \cdot \xi_2 / \xi_1$ . A similar mathematical treatment evaluated solely over

the spatial domain for CW laser heating is shown in **Figure 3b** where  $\xi_1 = \int_0^V I dv$  and

$$\xi_2 = \int_0^V I \Delta T dv .$$



**Figure 3.** Illustration of the sample surface temperature and laser spot intensity that compose the Raman weighted temperature and subsequent Raman shift power coefficient  $\psi$  for the ns and CW laser heating and Raman probing. (a) The time progression of the laser spot intensity  $I$ , surface temperature  $\Delta T$ , and corresponding Raman weighted temperature  $I \times \Delta T$  during a single ns laser pulse. The intensity and Raman weighted temperatures are both shown as integrals over the spatial and time domain,  $\xi_1$  and  $\xi_2$ , which are divided to represent the Raman shift coefficient  $\psi_{ns}$ . (b) The laser spot intensity and Raman weighted temperatures for the CW cases are simply integrated over the spatial domain. Their ratio determines the Raman shift power coefficient  $\psi_{CW}$ .

### 2.3 Radiative Recombination Probing: Physics

Here it is worth noting the differences in absorbed laser energy distribution between the three energy transport states. For all three lasers (CW, ns, and ps) the incoming incident photon energy  $E = 2.33 \text{ eV}$  is greater than the bandgap energy of monolayer WSe<sub>2</sub>  $E_g = 1.67 \text{ eV}$ <sup>33</sup>.

Photoexcited electrons lose this excess energy ( $E - E_g$ ) by direct phonon emission during fast thermalization adding to the nonradiative energy contribution in the sample. The majority of these photoexcited electrons then recombine with holes across the bandgap  $E_g$  via nonradiative recombination. However, a finite percentage of excited electrons recombine radiatively by emitting photons. We will define the percentage of absorbed photon energy ascribed to radiative recombination of electrons-hole pairs as  $\beta E_g$  where  $\beta$  is the radiative recombination efficiency. Therefore, during laser excitation the total absorbed energy converted to nonradiative processes becomes  $E - E_g + (1 - \beta)E_g$ .

In our picosecond energy transport state, introducing a picosecond pulsed laser (13 ps laser pulse width) distinguishes the nonradiative recombination heating effect  $(1 - \beta)E_g$  from the fast thermalization energy contribution  $E - E_g$  allowing for characterization of the radiative recombination efficiency  $\beta$ . This is because the 13 ps pulse width is much shorter than the recombination lifetime of excitons in monolayer WSe<sub>2</sub> which has been observed to be 4 ns<sup>30</sup>. In other words, during the ps laser pulse, the only energy contributed to the system comes from  $E - E_g$  converted to thermal energy since nonradiative recombination has not occurred yet – detailed description is shown **Figure 2d**. The nonradiative recombination effect from  $(1 - \beta)E_g$  has much less of an impact on the accumulated heating of the sample and the measured

temperature rise during the picosecond pulse. On the other hand, the CW and ns cases have greater dependence on the accumulated heating effect from nonradiative recombination. The differentiated energy contributions between the multiple energy transport mechanisms – steady state and near-zero transport (**Figure 2c**) – distinguish the radiative recombination effect in 2D monolayer materials.

To experimentally determine the radiative recombination efficiency, laser heating and Raman probing of the WSe<sub>2</sub> monolayers with the ps laser yield a new Raman shift coefficient  $\psi_{ps}$ . This laser power differential can be divided by the CW reference  $\psi_{CW}$  to form a normalized RSC:  $\Theta_2 = \psi_{ps} / \psi_{CW}$ . Note that once again, taking the ratio of these separate Raman shift coefficients eliminates the effect from laser absorption and Raman temperature coefficient. Therefore,  $\Theta_2$  can be equated to the ratio of the temperature rises from CW and ps laser heating:

$$\Delta T_{ps} / \Delta T_{CW}.$$

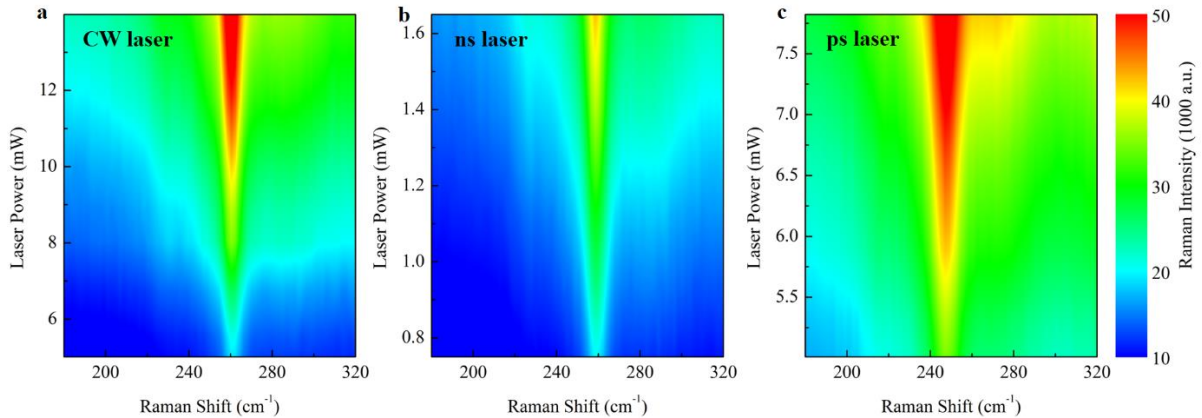
Next, two distinct numerical simulations of the heat transfer during ps heating are done: one to simulate the temperature rise induced by accumulated heating at the substrate ( $\Delta T_0$ ) and another to simulate the temperature rise in the monolayer sample from a single ps laser pulse ( $\Delta T_1$ ). Since the single ps pulse heating only involves a fractional amount of the total thermal energy involved in overall system heating, it becomes possible to introduce the factor  $(E - E_g) / [E - E_g + (1 - \beta)E_g]$  to the temperature rise  $\Delta T_1$ . This term represents the percentage of thermal energy contribution from direct phonon emission during fast thermalization.

Therefore,  $\Delta T_{ps}$  can be written in terms of the radiative recombination efficiency  $\beta$  and solved for based on the measured ratio  $\Theta_2$ .

## CHAPTER 3. EXPERIMENTAL RESULTS

### 3.1 Interfacial Thermal Conductance Determination

A LabView computer program automatically adjusted a neutral density optical filter to vary the laser power eight to twelve times during room-temperature Raman measurements. A CCD (charge-coupled-device) camera (Olympus DP-26, Olympus Optical Co., Ltd.) captured an image of the laser spot on the sample surface. The spatial energy distribution from the incident lasers (CW, ns and ps) on the sample surface is characterized by a Gaussian function and can be derived from the image data. The laser spot radius is calculated at  $e^{-1}$  of the peak intensity. The radius from the image data is used during numerical modeling to simulate as accurately as possible the temperature rise in the sample. The approximate radii for each laser are given as follows:  $r_0 = 1.9 \text{ } \mu\text{m}$  (CW),  $r_0 = 1.0 \text{ } \mu\text{m}$  (ns),  $r_0 = 1.6 \text{ } \mu\text{m}$  (ps). In the time domain the three lasers have distinct intensity distributions. The CW laser continuously emits light while the ns and ps lasers emit light in periodic pulses with defined repetition rates: 300 kHz and 48.2 MHz for the ns and ps lasers, respectively. This translates into a 200 ns pulse width at 3  $\mu\text{s}$  intervals for the ns laser and a 13 ps pulse width at 20.8 ns intervals for the ps.

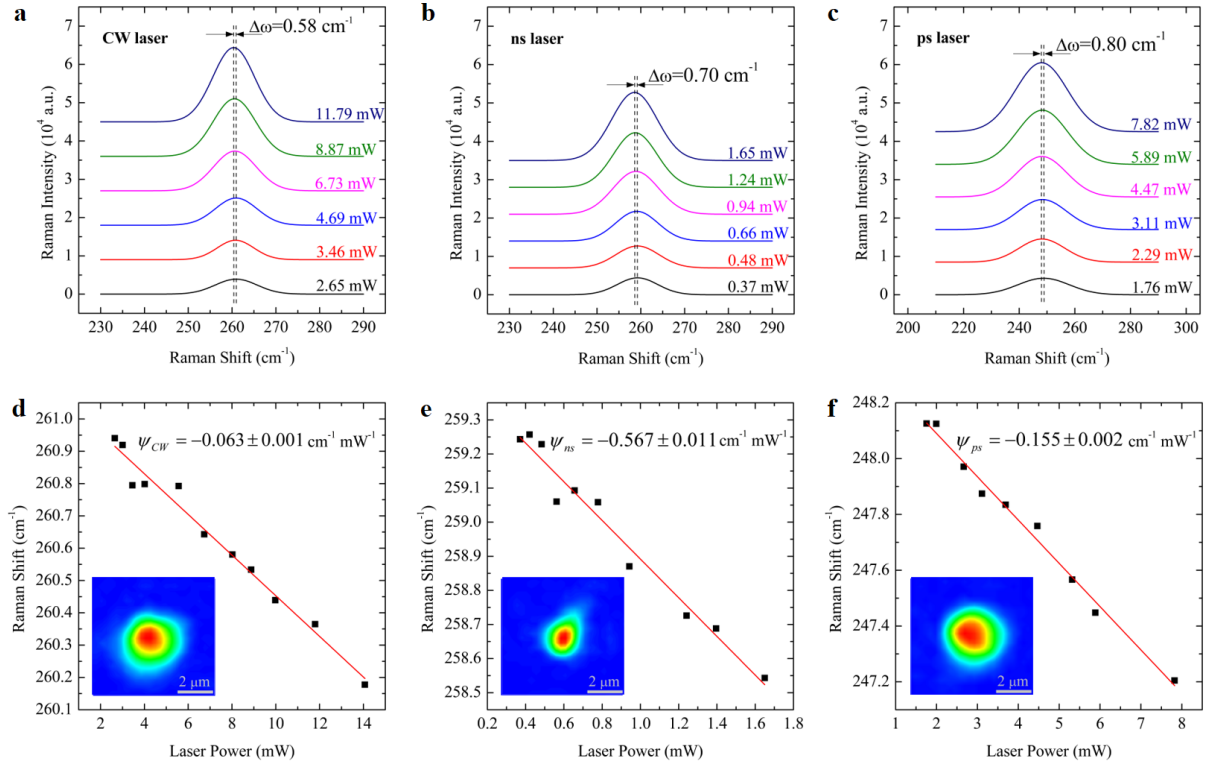


**Figure 4.** 2D contours of the laser-dependent peak Raman intensities for the degenerate  $A_{1g}$  and  $E_{2g}^1$  first order vibrational modes near  $250 \text{ cm}^{-1}$ . (a)-(c) show the increasing intensity as the laser power increases for all three laser heating cases: CW, ns, and ps.

The laser power incident on the sample after passing through the filter and the 20× objective lens ranged from 2.65 to 14.07 mW; 0.37 to 1.65 mW; and 1.76 to 7.82 mW for the CW, ns, and ps lasers, respectively. **Figure 4a-c** shows the 2D contour map of WSe<sub>2</sub> Raman peak intensity of a single representative monolayer sample (sample #5) – the sample that will be used to discuss experimental results ( $G$  and  $\beta$  values were evaluated for a total of five samples). The Raman intensity of the degenerate  $A_{1g}$  and  $E_{2g}^1$  peak increases with laser power. Although the Raman shift change against the laser power is small, this trend is still evident in **Figure 4**. To precisely determine the Raman shift change with the laser power, precise determination of the Raman peak location is needed by peak fitting. Six representative room temperature Raman spectra at different laser powers are shown in **Figure 5a-c** for all three energy transport states; they show the small Raman shift change when the laser power is increased from low end to high end. This figure illustrates the Raman peak location redshift at increased laser powers. There is a balance between the experimental accuracy and physics consideration for the Raman shift change. A large Raman shift change is preferred to improve experimental accuracy, and a small temperature rise (Raman shift change) is needed to ensure the sample does not experience a high temperature rise that will result in physical property change or structural damage. The overall Raman shift change is controlled to be less than 1 cm<sup>-1</sup>, in our case around 0.8 cm<sup>-1</sup> or less. The power-dependent peak positions in the low power range are shown in the figure by using  $\Delta\omega = \omega(P_2) - \omega(P_1) = \psi(P_2 - P_1)$  where  $\psi$  is the RSC. Any aberrations in this linear relationship are derived from the uncertainties in Raman peak Gaussian fittings or the laser heating effect.

**Figure 5d-f** shows more clearly the linear relationship between Raman shift and laser power. The slope of the linear fitting represents the laser power differential we have denoted as the Raman shift coefficient  $\psi$  (i.e.  $\partial\omega/\partial P$ ). The RSC is proportional to the local temperature

rise of the sample. Moreover, the RSC represents the local temperature rise for unit laser power irradiation. For the representative sample being discussed, we obtain  $\psi$  values of  $-0.063 \pm 0.001$   $\text{cm}^{-1} \text{mW}^{-1}$ ,  $-0.57 \pm 0.01$   $\text{cm}^{-1} \text{mW}^{-1}$ , and  $-0.155 \pm 0.002$   $\text{cm}^{-1} \text{mW}^{-1}$  for the CW, ns, and ps cases, respectively. The three types of lasers induce distinct optical heating phenomena which make each  $\psi$  value unique. Furthermore, since each  $\psi$  is proportional to the same laser absorption coefficient and Raman temperature coefficient, taking the ratio of any of these RSC values cancels out these sample dependent variables.



**Figure 5.** Illustration of the Raman peak location dependency on laser power. (a)-(c) Six representative Raman spectrum as Gaussian fitted curves applied to the signal at  $250 \text{ cm}^{-1}$ . The peak location is slightly redshifted as laser power increases by  $0.58$ ,  $0.70$ , and  $0.80 \text{ cm}^{-1}$  for CW, ns and ps cases, respectively. (d)-(f) Raman shift locations of the WSe<sub>2</sub> signal plotted against laser power for all three laser scenarios. Note the negative linear relationship as laser power increases. The slope of the fitted line represents the Raman shift coefficient used to evaluate interfacial thermal resistance and radiative recombination efficiency. The bottom left insets show the Gaussian spatial energy distribution of the laser spot on the sample surface under the  $20\times$  objective lens for each respective laser.

To determine the interfacial thermal conductance, we begin with the normalized ratio of ns RSC to CW RSC:  $\Theta_1 = \psi_{ns} / \psi_{CW}$ . The normalized RSC  $\Theta_1$  becomes a function of local temperature rises of the WSe<sub>2</sub> monolayer sample alone from CW heating and ns heating. Note that the local temperature rises for both the CW and ns cases are Raman-intensity weighted

averages. In the CW case this is evaluated as:  $\bar{T}_{CW} = \int_0^V I e^{-z/\tau_L} T dv / \int_0^V I e^{-z/\tau_L} dv$  where  $I$  is the laser

intensity,  $T$  is the temperature at each point,  $V$  is the sample volume, and  $e^{-z/\tau_L}$  represents the intensity attenuation once the light enters the sample. For the monolayer samples studied in this work, such intensity attenuation become negligible, but will be important for thick (e.g. tens of nm) samples. Note that the temperate at any point on the sample is governed by the basic equation relating the temperature difference across an interface to the resistance of heat transfer

across it:  $T_{WSe_2} = R_{tc}'' q'' + T_{SiO_2}$  where  $q''$  is local heat flux at the interface and  $T_{SiO_2}$  is the substrate

surface temperature. Due to the extremely thin thickness of the sample, the in-plane heat conduction and hot carrier diffusion effect is negligible compared with the local interface energy transport. Thus, it can be shown that the Raman-intensity weighted average reduces to

$\bar{T}_{CW} = a R_{tc}'' I_0 / 2 + \bar{T}_{s,CW}$  where  $R_{tc}''$  is the interfacial thermal resistance,  $a$  is the laser absorption,

$I_0$  is the incoming laser peak intensity (assuming unit 1 mW irradiation where the laser intensity

has a Gaussian distribution of  $I = I_0 \exp(-r^2 / r_0^2)$ ), and  $\bar{T}_{s,CW}$  is the Raman-intensity weighted

average temperature rise of the substrate under CW heating. In the ns case, the average must be

integrated over the space and time domain:  $\bar{T}_{ns} = \int_0^t \int_0^V I e^{-z/\tau_L} T dv dt / \int_0^t \int_0^V I e^{-z/\tau_L} dv dt$ . This equation

can similarly be reduced to  $\bar{T}_{ns} = a R_{tc}'' I_0 / (2\sqrt{2}) + \bar{T}_{s,ns}$  with  $\bar{T}_{s,ns}$  as the average temperature rise



of the substrate under ns heating and  $I_0$  as the incoming laser intensity for the ns laser. Note that the above weighted averages for temperature rises in both CW and ns cases only involve one unknown: the interfacial thermal resistance  $R_{ic}''$ .

The above treatment has significance for the 3D modeling of heat conduction in the sample structure. Since the WSe<sub>2</sub> sample is so thin (~1 nm), normal modeling would require a large number of meshes and take a very long time to simulate a physically reasonable domain size of ~10  $\mu\text{m}$  using a variable mesh starting from <1 nm in WSe<sub>2</sub>. In our modeling, first of all, we model the heat conduction in the substrate to obtain its temperature rise under CW and ns laser heating situations ( $\bar{T}_{s,CW}$  and  $\bar{T}_{s,ns}$ ) with surface heat flux boundary conditions. Then the temperature rise of the WSe<sub>2</sub> layer is calculated using the above equations. In the modeling, the optical absorption depth of WSe<sub>2</sub> is calculated using  $\tau_L = \lambda / 4\pi k_L$  where  $\lambda = 532 \text{ nm}$  is the laser wavelength and the extinction coefficient  $k_L = 1.28$  is used from reference values<sup>34,35</sup>. Note, accuracy of the absorption depth will not affect the final interface thermal conductance determination since the absorption coefficient is canceled out during the temperature rise ratio calculation. Then, since  $\psi_{CW}$  and  $\psi_{ns}$  are proportional to the average temperature rises of the WSe<sub>2</sub> monolayer sample under each laser heating scenario, respectively, the normalized RSC  $\Theta_1 = \psi_{ns} / \psi_{CW}$  can be equated to the temperature rise ratio  $\bar{T}_{ns} / \bar{T}_{CW}$ . Thus, the interfacial thermal resistance becomes entirely dependent on the experimentally determined  $\Theta_1$ . The only other relevant parameters used in modeling are the volumetric heat capacities of WSe<sub>2</sub> ( $\rho c_p = 1.98 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ ) and glass ( $\rho c_p = 1.65 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ ) as well as the thermal conductivity of glass ( $k = 1.4 \text{ W m}^{-1} \text{ K}^{-1}$ )<sup>32,36</sup>.

For sample #5 the normalized RSC is evaluated as  $\Theta_1 = 9.01 \pm 0.22$ . **Figure 6a** shows how  $\Theta_1$  changes with interfacial thermal conductance. With the experimentally measured ratio  $\Theta_1$ , we can precisely determine the corresponding interfacial conductance  $G$ . For the given value of  $\Theta_1$ , the interfacial thermal conductance is  $6.49 \pm 0.58 \text{ MW m}^{-2} \text{ K}^{-1}$ . The uncertainty determination based on the uncertainty of  $\Theta_1$  is also included in **Figure 6a**. In this work, we have measured five samples. The  $G$  values for all five measured samples along with the relevant parameters are summarized in **Table 1**. Discussion about the data will be given in Chapter 4.

**Table 1.** *The Raman shift laser power coefficients (RSC) for the CW and ns cases along with the normalized RSC and corresponding interfacial thermal conductance.*

Sample Number	$\psi_{CW} \text{ (cm}^{-1} \cdot \text{mW}^{-1})$	$\psi_{ns} \text{ (cm}^{-1} \cdot \text{mW}^{-1})$	$\Theta_1$	$G \text{ (MW} \cdot \text{m}^{-2} \cdot \text{K}^{-1})$
1	$-0.064 \pm 0.002$	$-0.36 \pm 0.03$	$5.61 \pm 0.23$	$15.9 \pm 5.0$
2	$-0.052 \pm 0.001$	$-0.57 \pm 0.01$	$11.0 \pm 0.3$	$2.10 \pm 0.14$
3	$-0.051 \pm 0.002$	$-0.55 \pm 0.01$	$10.8 \pm 0.4$	$4.21 \pm 0.47$
4	$-0.056 \pm 0.002$	$-0.51 \pm 0.01$	$9.16 \pm 0.33$	$8.14 \pm 1.24$
5	$-0.063 \pm 0.001$	$-0.57 \pm 0.01$	$9.01 \pm 0.22$	$6.49 \pm 0.58$

### 3.2 Radiative Recombination Efficiency Determination

Once the interfacial thermal conductance has been determined, we can apply the ps Raman shift coefficient  $\psi_{ps}$  to determine the radiative recombination efficiency  $\beta$ . For the sample under discussion (sample #5),  $\psi_{ps} = -0.155 \pm 0.002 \text{ cm}^{-1} \text{ mW}^{-1}$ . The normalized RSC taken as  $\Theta_2 = \psi_{ps} / \psi_{CW}$  becomes  $2.47 \pm 0.05$ . This ratio is equivalent to the ratio of Raman-intensity weighted temperature rises calculated from numerical modelling:  $\bar{T}_{ps} / \bar{T}_{CW}$ . It is important to note that  $\bar{T}_{ps}$  is composed of numerical temperature rises from 1) accumulated

steady state heating at the substrate interface ( $\Delta T_0$ ) and 2) single pulse near-zero transport heating in the WSe<sub>2</sub> monolayer ( $\Delta T_1$ ). The accumulated temperature rise of the substrate is calculated assuming 1 mW unit laser power irradiation. The absorbed laser energy is converted to thermal energy with a percentage of  $[E - E_g + (1 - \beta)E_g] / E$  in the physical process. Here  $E$  is the laser photon energy (2.33 eV) and  $E_g$  is the WSe<sub>2</sub> bandgap (1.67 eV). CW and ns simulations similarly assume 1 mW laser irradiation with the same thermal energy contribution. Note that the 1 mW laser irradiation assumption for the simulations is feasible and does not affect our results because we take the ratio of temperature rises to form the RSC.

Considering the single ps pulse heating effect, the atomically thin monolayer WSe<sub>2</sub> will not have 1 mW laser absorption. This is because the optical absorption depth of monolayer WSe<sub>2</sub> ( $\tau_L = 33$  nm) is much greater than the sample thickness ( $\Delta z = 0.7$  nm); only a small fraction of the 1 mW unit laser power is absorbed in the sample. It is important to note that the absorbed energy can only be converted to thermal energy  $E - E_g$  because it occurs at the time scale of the 13 ps pulse – much earlier than e-h recombination. Thus, the temperature rise from single pulse heating  $\Delta T_1$  results from a percentage of the absorbed laser energy as  $(E - E_g) / E$ .

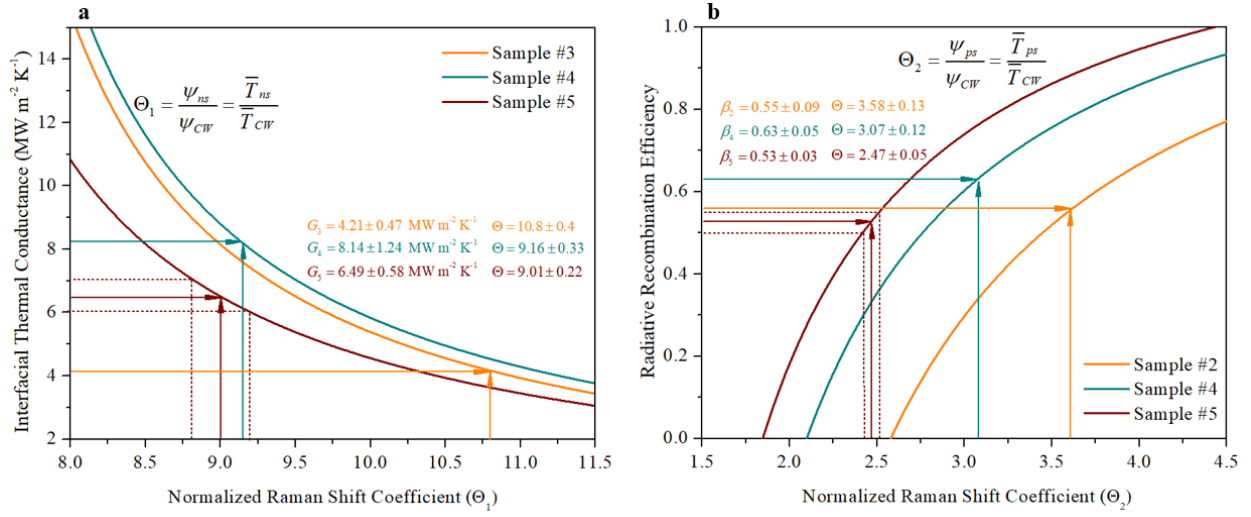
Note that the thickness of single layer WSe<sub>2</sub> has been reported as  $\sim 0.7$  nm<sup>37</sup> and  $\sim 1.1$  nm<sup>38</sup> based on AFM measurements. In our modeling we use the former value because it matches our own AFM measurement. We could have easily chosen the latter since sample thickness dependence is nullified during Raman shift coefficient ratio analysis. The combined heating effect due to accumulated and pulse heating can then be summarized by the overall temperature rise  $\bar{T}_{ps} = \Delta T_0 + \Delta T_1$  where  $\beta$  is the only unknown. Finally,  $\beta$  can be solved for based on the experimentally measured ratio  $\Theta_2$ . For the sample (sample #5) being considered,

$\Theta_2 = 2.47 \pm 0.05$  which corresponds to a radiative recombination efficiency of  $0.53 \pm 0.03$ . The results for all five samples are shown in **Table 2**. **Figure 6b** demonstrates how the normalized RSC  $\Theta_2$  changes for different values of  $\beta$ . The experimentally measured  $\Theta_2$  identifies the radiative recombination efficiency of the WSe<sub>2</sub> sample. The uncertainty determination for  $\beta$  is also shown in the figure.

**Table 2.** *The Raman shift coefficients for the CW and ps cases along with the normalized RSC and corresponding radiative recombination efficiency  $\beta$ .*

Sample Number	$\psi_{CW}$ (cm <sup>-1</sup> ·mW <sup>-1</sup> )	$\psi_{ps}$ (cm <sup>-1</sup> ·mW <sup>-1</sup> )	$\Theta_2$	$\beta$
1	$-0.064 \pm 0.002$	$-0.120 \pm 0.002$	$1.89 \pm 0.06$	$0.36 \pm 0.06$
2	$-0.052 \pm 0.001$	$-0.186 \pm 0.005$	$3.58 \pm 0.13$	$0.55 \pm 0.09$
3	$-0.051 \pm 0.002$	$-0.162 \pm 0.004$	$3.18 \pm 0.12$	$0.65 \pm 0.07$
4	$-0.056 \pm 0.002$	$-0.171 \pm 0.004$	$3.07 \pm 0.12$	$0.63 \pm 0.05$
5	$-0.063 \pm 0.001$	$-0.155 \pm 0.002$	$2.47 \pm 0.05$	$0.53 \pm 0.03$

As can be seen in the tables, there is some slight variation between the measured  $G$  and  $\beta$  values for the five monolayer samples. Due to stage drift and the atomic-level thickness of the samples, the focal plane of the laser on the sample was not always the same during laser heating and Raman probing. This leads to slight inconsistencies in the location of the Raman shift signal which ultimately determines the laser power differential  $\psi$ . However, any inconsistencies will be factored out during the ratio analysis. The greatest source of uncertainty arises from the linear fitting itself. As evident in **Figure 5d-f**, not all data points match the fitting exactly. This linear fitting is based on the Raman peak positions of the Gaussian fitted curves applied to the degenerate vibrational modes near 250 cm<sup>-1</sup>. These theoretical curves are subject to non-negligible error that could impact the resulting  $G$  and  $\beta$  values.



**Figure 6.** The quantities of interest – interfacial thermal conductance  $G$  and radiative recombination efficiency  $\beta$  – behave as functions of their respective normalized Raman shift coefficient. The experimentally determined  $\Theta_1$  and  $\Theta_2$  identify the corresponding material property. Uncertainty values are shown for the representative sample #5 while samples #3 and #4 simply show the Raman shift coefficient curves with the corresponding temperature rise ratio. (a) For the measured RSC  $\Theta_1 = 9.01 \pm 0.22$  of sample #5 (i.e. the ratio of ns temperature rise to CW temperature rise), the corresponding  $G$  value is  $6.49 \pm 0.58 \text{ MW m}^{-2} \text{K}^{-1}$ . (b) For the measured RSC of  $\Theta_2 = 2.47 \pm 0.05$  (i.e. the ratio of ps temperature rise to CW temperature rise), the corresponding radiative recombination efficiency is  $\beta = 0.53 \pm 0.03$ . The graph shows results for samples #2, #4, and #5.

## CHAPTER 4. DISCUSSION OF EXPERIMENTAL RESULTS

### 4.1 Physics Interpretation of the Measured Interfacial Thermal Conductance

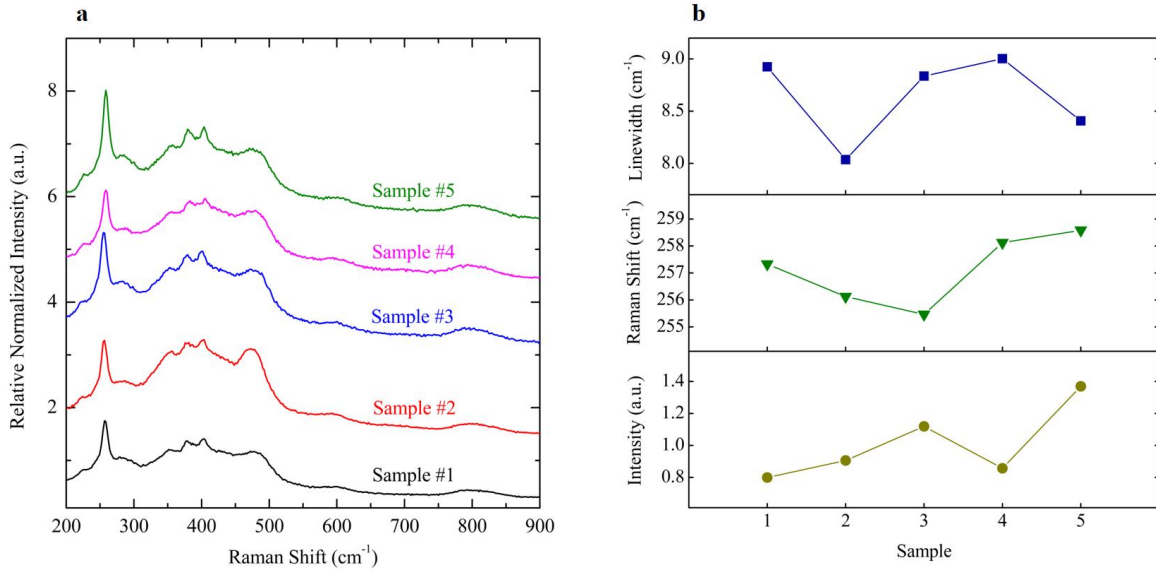
Many studies have explored interfacial thermal transport between MoS<sub>2</sub> and various substrates, including SiO<sub>2</sub>. Less research has been devoted to the interfacial thermal conductance of WSe<sub>2</sub>-based 2D structures. Vaziri *et al.* explored interface thermal conductance between heterogeneously layered 2D materials using Raman thermometry<sup>39</sup>. In a heterostructure stack of single layer graphene on top of a WSe<sub>2</sub> monolayer resting on a SiO<sub>2</sub> substrate, they observed thermal conductance across the WSe<sub>2</sub>/SiO<sub>2</sub> interface to be  $15 \pm 4 \text{ MW m}^{-2} \text{ K}^{-1}$ . Another study by Behranginia *et al.* examined the energy dissipation in few-layered WSe<sub>2</sub> field-effect transistors with thickness  $\sim 7 \text{ nm}$ <sup>40</sup>. Using low-frequency Raman thermometry and density functional perturbation theory (DFPT) to model phonon dispersion, they predict an interface thermal conductance between single layer WSe<sub>2</sub> and SiO<sub>2</sub> substrate as  $\sim 13 \text{ MW m}^{-2} \text{ K}^{-1}$ . These results are in close agreement with the measured  $G$  value for sample #1 in our own experiments ( $G = 15.9 \pm 7.0 \text{ MW m}^{-2} \text{ K}^{-1}$ ) and within a reasonable distance from the range of our other measured  $G$  values ( $2\text{-}8 \text{ MW m}^{-2} \text{ K}^{-1}$ ) for samples #2-5.

One possible explanation for the larger interfacial thermal conductance of sample #1, a noticeable outlier relative to the other samples, stems from laser heating damage at the beginning of Raman measurements. Structural changes in the sample induced by overheating could skew Raman peak location and intensity. Because the ET-Raman method depends on relative Raman shift location and Gaussian fitted curves, the resulting Raman shift coefficient would then carry non-negligible variation compared to that of an undamaged sample. Therefore, it is suspected that the larger, maximum laser power used during CW Raman measurements for sample #1 ( $\sim 30$

mW) compared to that of the other four samples (10-14 mW) altered the structural composition of the WSe<sub>2</sub> monolayer flake leading to a larger  $G$  value and uncertainty.

Furthermore, the sample-to-sample structure difference would explain the variation in interfacial thermal conductance between the five samples. Slight differences in the Raman spectrum between samples highlights the underlying sample structure diversity. The Raman spectrum of all five samples from ns laser probing is shown in **Figure 7a**. Note that the relative peak intensity of the 250 cm<sup>-1</sup> signal is not uniform across all five samples. More detailed analysis of the Raman peak characteristics for all five samples is shown in **Figure 7b**. This figure shows the Raman shift location, linewidth, and peak intensity of the signal for each measured monolayer. The peak intensity shows the most variation. This is most likely from distinct Raman intensity enhancement at the interfacial gap of each individual monolayer sample. Dissimilar spacing leads to distinct interfacial thermal transport which explains the modest range of values reported in this work. The spectra shown are normalized for laser power and integration time.

Comparing experimentally measured interfacial thermal conductance values with the peak intensity data from **Figure 7b** reveals a relation between the samples with the lowest Raman intensity and the highest conductance (samples #1 and #4). This makes sense because the larger conductance values will have small resistance and better interfacial contact. Less spacing between the substrate and monolayer means the Raman intensity enhancement due to reflections within the interfacial gap is reduced and the resulting intensity decreases. This relation between peak intensity and  $G$  does not hold true for the other three samples because the inherent structural properties of the WSe<sub>2</sub> crystal also play a critical role in Raman signal intensity.



**Figure 7.** Raman spectra comparison of all five samples from ns laser probing. (a) Plotted Raman spectra where the intensity axis is normalized to account for laser power and integration time, both slightly adjusted over the course of ET-Raman measurements to extract a reliable Raman shift coefficient. (b) The peak intensity, Raman shift location, and linewidth of the WSe<sub>2</sub> Raman signal for each sample. Note that the WSe<sub>2</sub> characteristic peak around 250 cm<sup>-1</sup> is not identical across the five monolayer samples. Direct comparison of the Raman signal characteristics illustrates the unique structural composition of each sample. The maximum percent difference across all five samples is 53% for peak intensity, 11% for linewidth, and 1.2% for Raman shift. The moderate differences between samples suggests the crystal structure and interface bonding are not identical which would lead to slight differences in interfacial thermal conductance and radiative recombination efficiency.

The linewidth also shows moderate sample dependency. The Raman signal linewidth is related to the phonon lifetime with larger linewidths corresponding to shorter lifetimes and smaller linewidths corresponding to longer lifetimes. Because phonon lifetime is related to grain size in the crystal structure, the slight variation in linewidth suggests each sample could have marginally different structural compositions. The Raman shift changes between each sample show the least amount of variation. The sample diversity implies a sensible range of interface



bonding strengths and crystal structures which would explain the marginal range of interfacial thermal conductance values reported in this work.

For comparison, it is also worth discussing interfacial transport characteristics of similar 2D materials such as MoS<sub>2</sub> and WS<sub>2</sub>. Yalon *et al.* observed an interfacial thermal conductance of  $\sim 15 \text{ MW m}^{-2} \text{ K}^{-1}$  for CVD grown monolayer MoS<sub>2</sub> flakes on SiO<sub>2</sub> substrate at room temperature via Raman thermometry<sup>19</sup>. However, the difficulty of direct laser absorption measurements due to multiple light reflections at interfacial gaps required an estimation of absorption which could lead to unknown uncertainty in those final measurements. Another study by Yalon *et al.* using a similar Raman-based approach shows interface thermal conductance between monolayer MoS<sub>2</sub> and SiO<sub>2</sub> as  $14 \pm 4 \text{ MW m}^{-2} \text{ K}^{-1}$ <sup>41</sup>. Yu *et al.* used Raman thermometry techniques to measure  $G$  of 16-17 and 30  $\text{MW m}^{-2} \text{ K}^{-1}$  for single crystal MoS<sub>2</sub> and WS<sub>2</sub> monolayers on sapphire substrate, respectively<sup>42</sup>. They concluded that the strength of the interaction between 2D TMDs and substrates strongly influences the interfacial thermal conductance; transferring as-grown MoS<sub>2</sub> monolayer flakes to a separate sapphire substrate resulted in a 40-50% drop in measured  $G$ . The group also observed an interfacial thermal conductance of  $18.6 \text{ MW m}^{-2} \text{ K}^{-1}$  for single crystal MoS<sub>2</sub> monolayers on SiO<sub>2</sub>/Si substrate.

In all the aforementioned studies, the radiative recombination of generated electron-hole pairs has not been considered. The assumption that all the absorbed energy in the monolayer sample is converted to thermal energy fails to account for the considerable proportion of energy converted to light when electrons recombine with holes and release energy through photon emission. Thus, this overestimated absorbed energy would lead to larger interfacial thermal conductance values. The ET-Raman method circumvents this problem of overestimated energy

absorption by nature of the ratio analysis through which the absorbed laser energy is cancelled out. This explains the lower range of conductance value results determined in this study.

Furthermore, most studies explore interfacial conductance between TMD monolayers and thermally grown silicon dioxide substrate. Fewer studies have been done with fused silica substrates. Thermally grown silicon dioxide has smaller surface roughness relative to fused silica. To illustrate this point, fused silica RMS surface roughness ( $\delta$ ) measures 0.4 nm after a combination of washing with basic peroxide and then acidic peroxide<sup>43</sup>. Additionally, even after CO<sub>2</sub> laser polishing, fused silica has a measured surface roughness ( $Ra$ ) up to 25 nm<sup>44</sup>. For comparison, in Si/SiO<sub>2</sub> substrates as oxide growth reaches 10 nm thickness during oxidation, surface roughness ( $\delta$ ) reaches a maximum around 0.12 nm<sup>45</sup>. The minimum possible difference between these reported roughness values is 28% of the WSe<sub>2</sub> monolayer thickness meaning surface roughness effects become much more pronounced at the atomic scale. It has been well documented that surface roughness decreases overall thermal transport across an interface<sup>9</sup>. This is because when the RMS roughness  $\delta$  becomes larger than the phonon wavelength, interface roughness more strongly affects phonon transport<sup>46</sup>. In other words, when the phonon wavelength is larger than the interface roughness, the phonon can pass through the rough region as if it were not present. Phonons with wavelengths smaller than  $\delta$  are more likely to attenuate passing through the interface. Therefore, the greater surface roughness of the fused silica substrate used in our samples would also explain the lower range of interfacial thermal conductance values reported in this work.

In our previous works we demonstrated an order of magnitude difference in interface thermal conductance in few-layered MoS<sub>2</sub> due to interface surface effects. Applying the ET-Raman technique to characterize seven MoS<sub>2</sub> samples (6.6–17.4 nm) on c-Si, the interfacial

thermal conductance values were measured in the range of  $5\text{--}8 \text{ MW m}^{-2} \text{ K}^{-1}$ <sup>29</sup>. Similar sized MoS<sub>2</sub> samples ranging from 1.8 to 18.0 nm supported by an unpolished glass substrate were reported to have interfacial thermal conductance values in the order of  $\sim 0.5 \text{ MW m}^{-2} \text{ K}^{-1}$ <sup>47</sup>. This one order of magnitude difference can be explained by the imperfect contact between the unpolished glass and the 2D material. When the MoS<sub>2</sub> sample is loosely supported by the high points of the glass substrate the interfacial thermal conductance decreases. A 2D sample supported by a less rough substrate surface such as c-Si enhances interface energy coupling due to the better contact between the adjacent materials leading to larger  $G$  values. These examples support our claim that relatively rough substrate surfaces, such as the fused silica in our experiments, can dramatically lower interfacial thermal conductance.

#### 4.2 Discussion on Electron-hole Recombination

The radiative recombination efficiency, also known as internal quantum efficiency (IQE) or photoluminescence quantum yield (PL QY), of TMD 2D materials has received significant attention because of the enhanced photoluminescence as single atomic layers. Salehzadeh *et al.* observed an IQE of 8.3% in mechanically exfoliated single layer MoS<sub>2</sub> on Si/SiO<sub>x</sub> substrate at room temperature via power-dependent photoluminescence studies and rate equation analysis<sup>48</sup>. They determine that Shockley-Read-Hall recombination and indirect Auger scattering reduce the maximum allowable IQE for MoS<sub>2</sub> light-emitting devices. Liu *et al.* observed an IQE of 6.35% for single layer CVD-synthesized WS<sub>2</sub> on sapphire substrate through transient absorption measurements under pulsed laser irradiation<sup>49</sup>. In addition, it has been shown that as-exfoliated and as-grown CVD-synthesized WSe<sub>2</sub> monolayers on fused silica substrate exhibit quantum yield of  $\sim 2\%$ <sup>50</sup>.

Other works have detailed how to increase the PL QY of monolayer TMDs through chemical treatment or electrostatic doping. Amani *et al.* developed an organic superacid

treatment using bis(trifluoromethane) sulfonimide (TFSI) to vastly improve the PL QY of sulfur-based single layer TMDs on quartz substrates to near unity performance <sup>51</sup>. Before treatment, they found maximum quantum yield of as-exfoliated monolayers to be at or below 5% for MoS<sub>2</sub>, WSe<sub>2</sub>, and MoSe<sub>2</sub> and at nearly 20% for WS<sub>2</sub>. Lien *et al.* discovered that electrical suppression of nonradiative pathways via electrostatic doping increases radiative recombination in MoS<sub>2</sub> and WS<sub>2</sub> while decreasing quantum yield for WSe<sub>2</sub> <sup>52</sup>. Before doping, they measured a quantum yield of 8% for single layer WSe<sub>2</sub>. These experiments were done on Si/SiO<sub>2</sub> substrates.

It has become clear that interactions at the 2D material-substrate interface significantly influence luminescence efficiency for TMD monolayers. These effects include induced strain, dielectric screening, and doping – with doping from the substrate as the primary facilitator of defect-assisted nonradiative recombination <sup>8</sup>. Furthermore, the bonding strength between substrate and 2D material also dictates overall radiative recombination efficiency. Kim *et al.* demonstrated that strong coupling between substrate and single layer WSe<sub>2</sub> diminishes maximum achievable PL QY <sup>53</sup>. By using a solvent evaporation-mediated decoupling (SEMD) technique – an evaporating solvent causes surface tension to release the grown monolayer from the substrate – they observe quantum yield up to ~60% for CVD-grown WSe<sub>2</sub> monolayers decoupled from fused silica substrates. Before decoupling, the same monolayers only exhibited ~1% PL QY.

The radiative recombination efficiency values reported in this work range from 36% to 65% – larger than most reported values for untreated WSe<sub>2</sub> monolayers (below 8%). However, it is important to note the novel method used to synthesize the 2D crystals used in this work. The studies previously mentioned used CVD-grown WSe<sub>2</sub> monolayers which have strong interactions with their substrates. Until this time, the radiative recombination efficiency of high-quality laser-

assisted synthesized (LAST) TMD crystals has not been measured. Notably, monolayers synthesized via LAST have lower levels of impurities compared to materials grown via CVD<sup>24</sup>. Thus, defect-assisted nonradiative recombination is reduced leading to higher levels of radiative recombination. Therefore, it is reasonable to assume that the larger radiative recombination efficiencies measured from our experiments could be partially explained by the low-density of impurities in the WSe<sub>2</sub> monolayer flakes. Further analysis of the thermal and optical properties of 2D materials fabricated by other laser-based synthesis methods such as self-limiting laser crystallization (SLLC)<sup>54</sup> would help identify differences between thin film fabrication techniques.

## CHAPTER 5. CONCLUSION AND FUTURE WORK

### 5.1 Conclusion

In this work, an energy transport state-resolved Raman (ET-Raman) method was employed to determine the interfacial thermal conductance and radiative recombination efficiency of supported WSe<sub>2</sub> monolayers on fused silica substrate. This technique constructed and probed steady, nanosecond, and picosecond energy transport states, and was able to distinguish the effect of radiative recombination. It did not require Raman temperature calibration or laser absorption coefficients which introduce unknown error to experimental results. Five monolayer samples were irradiated with a CW and ns laser to simultaneously heat the sample and measure the Raman signal. Raman shift power coefficients were derived from the experimental data and used in conjunction with 3D numerical modeling to determine the temperature rise and corresponding interfacial thermal conductance of the samples. The interfacial thermal conductance values range from 2 – 16 MW m<sup>-2</sup> K<sup>-1</sup>. The lower range of reported values in this work were attributed to the decreased interface energy coupling caused by the relatively rough surface of the fused silica substrate and novel thin film fabrication method. Furthermore, this work is one of the first to consider the effect of radiative e-h recombination on thermal transport characteristics of monolayer TMDs. Neglecting radiative recombination leads to an overestimation of absorbed laser energy contributing to larger interfacial thermal conductance values. To determine the radiative recombination efficiency, a ps laser was introduced to define a new Raman shift coefficient. The numerical modelling for ps heating accounts for the ultrafast timescale of fast thermalization that precedes e-h recombination. The determined temperature rise evaluated from modeling is then related to the CW and ps Raman shift coefficients to determine the radiative recombination efficiency. The efficiency values for

the five monolayer samples measured in this work range from 36-65%. The rate of radiative recombination determined in this work is higher than other reported values for CVD-grown TMD monolayers. The discrepancy from other works can be explained by the high quality TMD monolayers fabricated via a novel laser-based synthesis method (LAST); lower levels of impurities in the 2D material restrict pathways for nonradiative recombination while enhancing radiative recombination. Additionally, weaker coupling between the 2D material and substrate would enhance radiative recombination. Further studies to explore the bonding strength between LAST synthesized TMD monolayers with their substrate could also help clarify the substantial PL QY reported in this work.

## 5.2 Future Work

The results concluded in this thesis exemplify the fascinating thermal and optical properties of TMD 2D materials and their relationships with substrates. In future work it would be interesting to measure isolated phenomena involved in ET-Raman to more holistically understand thermal transport at the nanoscale for atomically thin TMD layers. In particular, it would be beneficial to examine effects related to substrate material and ns pulse width duration on interfacial resistance. It would also help to explore the radiative recombination of suspended monolayer samples.

As discussed in this work, the relatively rough surface of fused silica resulted in a larger interfacial thermal resistance between the TMD material and substrate when compared to similar samples on thermally grown silicon dioxide. In order to verify this measured difference future research would entail replicating the state-resolved ET-Raman method employed in this work to measure the resistance between LAST synthesized WSe<sub>2</sub> monolayers on thermally grown dioxide. It is expected that the resistance would be diminished due to the improved interfacial contact. However, as the interfacial thermal resistance effect becomes less pronounced in the

overall heating of the material-substrate system, it also becomes less sensitive to meaningful physical measurement through ET-Raman. Adjusting the pulsed laser temporal distribution could circumvent this problem.

Measurement sensitivity could serve as a future research topic of its own. This research would involve adjusting the ns laser pulse width to more closely align with the timescale of the nanoscale physics processes occurring at the 2D material-substrate interface. In our experiments the ns laser pulse width is set at 200 ns. This was chosen such that the interfacial resistance becomes comparable to the resulting substrate thermal resistance during pulse heating. Shortening the ns pulse width so that heat conduction across the interface contributes even more to the overall heating of the system enhances measurement sensitivity. A future project would involve taking multiple ET-Raman measurements to determine interfacial thermal resistance at different ns pulse widths. The results would help define how the laser pulse width affects the accuracy of experimental measurements.

Lastly, an exploration of the PL QY for suspended monolayer WSe<sub>2</sub> and other single layer TMDs could improve our understanding of the substrate effect on radiative electron-hole recombination. As has been established in the literature previously discussed, strong substrate bonding between the 2D material substrate can reduce overall radiative recombination. Removing the substrate from the equation by measuring suspended monolayers allows us to isolate this critical feature involved in electron-hole recombination and determine the degree to which substrates reduce PL QY.



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